UTILIZATION OF WASTE

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PRODUCTION OF CERAMIC PIGMENTS WITH WOLLASTONITE AND DIOPSIDE STRUCTURES USING NEPHELINE SLUDGE

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Ceramic pigments with wollastonite and diopside structures were obtained by using nepheline sludge in charge adjustment with magnesium and silicon oxides. The pigments are resistant to high temperatures and the effect of fluxes and glazes. They can be recommended to complement pigments of spectral colors and for bulk coloring of ceramic pastes and glazes. In addition to lowering the price of the pigments, problems of using nonutilizable production wastes are solved and the raw-material base for synthesis of ceramic pigments is expanded.

Materials in a wide color range are now required in modern construction. However, stable color can only be obtained as a result of addition of relatively expensive ceramic pigments. Synthesis of stable pigments using inexpensive raw material, industrial wastes, for example, whose utilization is an important problem, could be a solution to this problem.

Wollastonite and diopside ceramic pigments are obtained as a result of high-temperature, solid-phase synthesis either from pure chemicals or with natural concentrated wollastonite, $CaSiO_3$, and diopside, $CaMgSi_2O_6$, minerals with a high degree of purity [1 – 3].

We made ceramic pigments with wollastonite and diopside structures using waste from alumina production — nepheline sludge.

Nepheline sludge is the product of a complex, well regulated manufacturing process of processing natural nepheline-apatite ores and production of alumina, and the sludge is stable with respect to all properties [4]. Used nepheline sludge is now kept in dumps in large amounts, so that its subsequent processing is becoming a pressing problem. CaO and SiO_2, corresponding to a molar ratio of CaO : SiO_2 = 2 : 1 and constituting a total of 85 – 88%, are the basic chemical components of nepheline sludge.[2] The other oxides (Al_2O_3, MgO, Na_2O, K_2O) can be considered as minor components which have little effect on the structure and properties of the pigments obtained. The chemical composition of nepheline sludge from the Achinsk Alumina Combine is as follows (%): 29.12 SiO_2, 3.67 Al_2O_3, 4.55 Fe_2O_3, 53.20 CaO, 1.45 MgO, 2.16 Na_2O, 0.90 K_2O, 4.96 calcination loss. The mineral composition of nepheline sludge is basically represented by dicalcium silicate, and calcium hydrosilicates, hydroferrites, etc., are present as minor phases.

The presence of calcium and silicon oxides in nepheline sludge makes it possible to obtain ceramic pigments with wollastonite and diopside structures in charge adjustment with the corresponding oxides:

$$Ca_2SiO_4 + SiO_2 \rightarrow 2(CaSiO_3); \quad (1)$$

$$Ca_2SiO_4 + 3SiO_2 + 2MgO \rightarrow 2(CaMgSi_2O_6). \quad (2)$$

For synthesizing ceramic pigments, nepheline sludge was finely ground to a maximum residue of 2% on a No. 0063 sieve. Compounds of 3*d* elements: iron, chromium, nickel, and cobalt, added in the form of salts in the amount of 5 – 30% in oxide, were used as chromophores. In the reaction to obtain pigments with wollastonite structure, the chromophores were added to a mixture of nepheline sludge and silicon oxide, ensuring the stoichiometric composition of wollastonite. Diopside pigments were obtained by equimolecular substitution of magnesium oxide by oxide chromophores in the mixture, which ensured the

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[2] Here and below, unless specifically indicated otherwise, mass content.

TABLE 1

Pigment	Mass content, %						
	nepheline sludge	SiO_2	MgO	CoO	NiO	Cr_2O_3	Fe_2O_3
With the structure of wollastonite							
W-1	70.4	24.6	–	5.0	–	–	–
W-5	66.7	23.3	–	–	10.0	–	–
W-6	63.0	22.0	–	–	15.0	–	–
W-8	66.7	23.3	–	–	–	10.0	–
W-9	63.0	22.0	–	–	–	15.0	–
W-10	70.4	24.6	–	–	–	–	5.0
W-11	66.7	23.3	–	–	–	–	10.0
W-12	63.0	22.0	–	–	–	–	15.0
BS-1	74.1	25.9	–	–	–	–	–
With the structure of diopside							
D-1	38.9	40.7	15.3	5.1	–	–	–
D-2	38.3	40.0	13.4	8.3	–	–	–
D-5	38.3	40.0	13.4	–	8.3	–	–
D-6	36.8	38.5	8.6	–	16.1	–	–
D-7	36.9	38.7	14.6	–	–	9.8	–
D-8	35.2	36.9	12.3	–	–	15.6	–
D-10	36.7	38.5	14.5	–	–	–	10.3
D-11	34.9	36.6	12.2	–	–	–	16.3
BS-2	39.8	41.7	18.5	–	–	–	–

stoichiometric composition of diopside, according to the reaction:

$$Ca_2SiO_4 + 3SiO_2 + (2 - x)MgO + xMeO \rightarrow 2(CaMg_{(1-x)}Me_{(x)}Si_2O_6)$$

where $x = 0.3$, 0.5, and 1.0 mole.

The compositions of some pigments are reported in Table 1.

The pigments were fired at temperatures of 1000 – 1200°C. For the iron-containing pigments, the optimum color appeared at a firing temperature of 1100°C, and the pigments melted at higher temperatures. For cobalt- and nickel-containing pigments, a temperature of 1200°C, at which the brightest color formed, was optimum. Since nepheline sludge already contains a small amount (4.55%) of iron oxide, the goal was not to synthesize pigments of pure spectral colors. Actually, the palette of pigments obtained basically consists of pale and subdued hues. The blank samples were cream colored according to reaction (1) and light yellow with reaction (2).

The pigments obtained with reactions (1) and (2) with the same chromophore had different shades. They were applied on the ceramic articles as underglaze colors. The color of the pigments and colors is given in Table 2. The pigments were stable in underglaze painting and almost did not change color.

TABLE 3

Pigment	Chromaticity coordinates		Wavelength, nm	Purity of tone, %
	X	*Y*		
D-2	0.38	0.31	496	13
W-8	0.36	0.39	569	34
D-8	0.38	0.40	574	45
W-11	0.51	0.37	597	69
D-11	0.54	0.35	605	70

The x-ray phase analysis showed (see Fig. 1) that the pigments obtained with reaction (1) had a wollastonite structure ($d = 0.323$, 0.297, 0.280 nm) and the pigments synthesized with reaction (2) had a complex composition: diopside ($d = 0.323$, 0.299, 0.256 nm), wollastonite ($d = 0.775$, 0.407, 0.383 nm), and akermanite ($d = 0.351$, 0.287 nm) were identified in them. On addition of 8 – 10% nickel oxide in the wollastonite and diopside pigments, the oxide was identified in the x-ray patterns in the form of an independent phase. Iron oxide was completely embedded in the structure and was not separated in free form in synthesis of wollastonite pigments. Small diffraction peaks characteristic of this oxide ($d = 0.368$, 0.269, 0.221 nm) were observed in the x-ray patterns of the iron-containing diopside pigments with a greater than 10% Fe_2O_3 content.

The spectral reflection curves used to calculate the color index coordinates were made on an SF-18 spectrophotometer. The dominant wavelength and purity of the pigment hue were determined. The color characteristics of some pigments are reported in Table 3.

TABLE 2

Ion chromophore	Wollastonite structure, reaction (1)		Diopside structure, reaction (2)	
	color of pigment at firing temperature of 1100°C	underglaze color at firing temperature of 1050°C	color of pigment at firing temperature of 1100°C	underglaze color at firing temperature of 1050°C
Fe^{3+}	Orange-brown	Yellow-brown	Brick red	Red-brown
Cr^{3+}	Light green	Lettuce green	Olive green	Grey-green
Ni^{2+}	Grey	Brown	Light beige	Yellow-lettuce green
Co^{2+}	Black	Grey	Grayish lilac	Lilac
BS	Yellowish beige	Light yellow	Light beige	Colorless

Use of nepheline sludge for obtaining ceramic pigments with different crystal structures is thus economically expedient. The synthesized pigments are resistant to high temperatures and flux and glaze melts. They can be recommended to supplement pigments of spectral colors and of bulk coloring of ceramic pastes and glazes.

The pigment compositions developed can be widely used for manufacturing colored construction materials. In addition to reducing the cost of the pigments, problems of

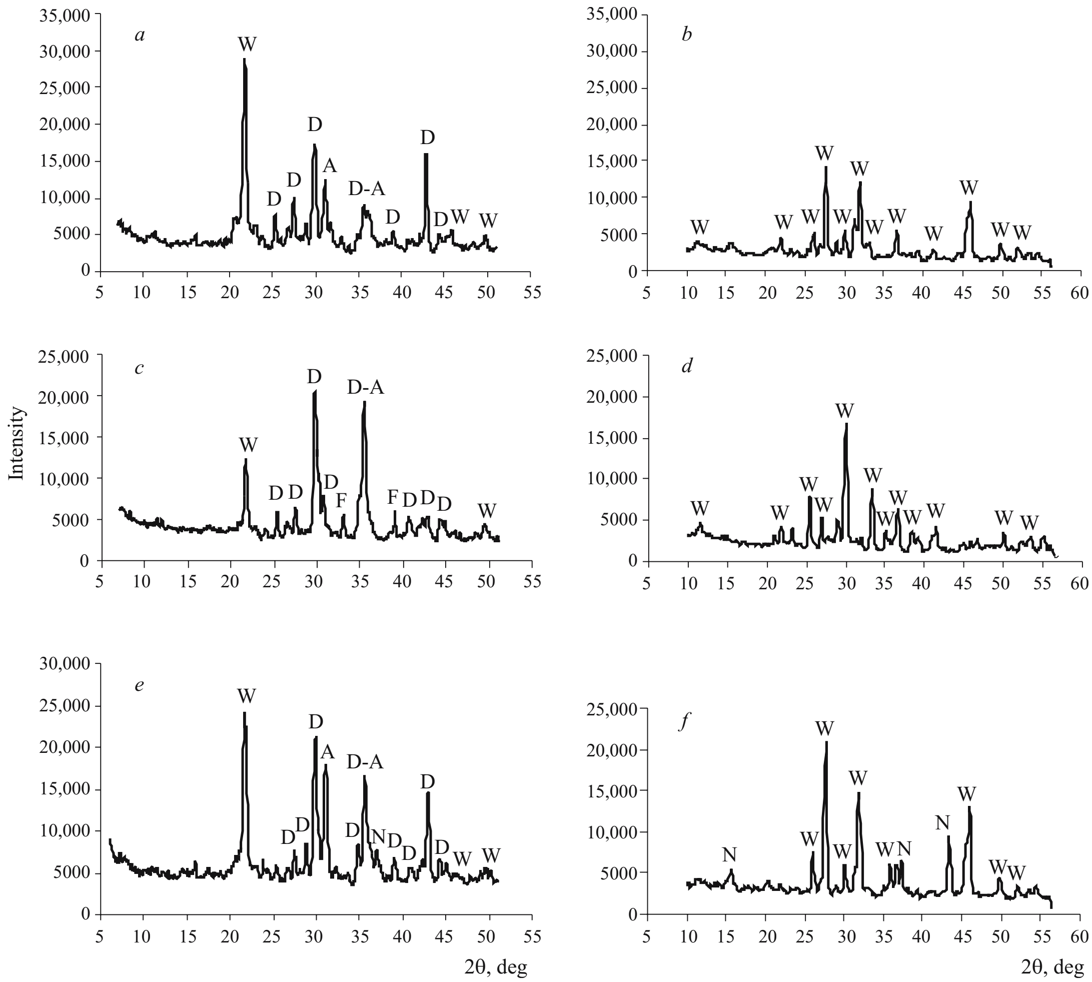

Fig. 1. X-ray patterns of blank samples (*a*, *b*) and pigments D-11 (*c*), W-10 (*d*), D-5 (*e*), and W-5 (*f*): *1* and *2*) according to reactions (1) and (2), respectively; W) wollastonite; D) diopside; A) akermanite; F) Fe_2O_3; N) NiO.

utilizing nonutilizable production wastes can be solved and the raw-material base for synthesis of ceramic pigments can be expanded.

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